Stationary flows in quantum dissipative closed circuits as a challenge to thermodynamics

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(Dated: October 3, 2001)

Abstract

Existence of stationary flows in quantum non-dissipative closed circuits is not surprising - diamagnetic currents in atoms are one of such examples. Here, a model is constructed and rigorously solved from the Hamiltonian level where such a dc circular spontaneous flow exists in absence of a magnetic field, irrespective of presence of dissipation causing otherwise proper relaxation. The flow causes a spontaneous unidirectional transfer of heat from one bath to another one, even against temperature step. This is what is explicitly forbidden by the Clausius form of the Second law of thermodynamics. The unidirectionality of the flow is caused by that of spontaneous processes known to bear this property since their introduction by Einstein. The model slightly improves the previous one (Capek & Sheehan 2001), describes a realistic system for which experimental results violating the second law were announced, and fully supports the experimental conclusions (Sheehan 1995). All mathematical details are exposed, two independent types of mathematical arguments are invoked, and no approximations that could be made responsible for the striking conclusions are used. It shows how little the physics beyond the Second law is still understood.

PACS numbers: 05.30.-d, 05.70.-a, 44.90.+c

Keywords: 2^{nd} Law Challenge

I. INTRODUCTION

Challenges to the second law of thermodynamics [1, 2] are almost as old as the law itself, dating back at least to the 1870's with Maxwell's celebrated demon [3, 4, 5, 6]. Most of them have been resolved under close scrutiny [5, 7, 8] but some persisted. Anyway, strong belief in old authorities and natural human tendency to organize things and facts into closed logical units and complexes (scientific disciplines etc.) caused that almost nobody doubts about validity of standard thermodynamics, in particular the Second law, in at least the macroworld [9, 10]. Absolutistic statements like '...No exception to the second law of thermodynamics has ever been found - not even a tiny one...' [10] often appear and the second law is almost universally believed to be unquestionable. In our opinion, the situation is (perhaps still) not so clear. The reason is that experiments questioning the second law have been reported since 1995, have since been subject to a public discussion but remain so far unquestioned [11, 12].

In theory, arguments independent of these experiments appeared since 1997 [13] saying that in quantum systems with strong or at least intermediate coupling to its surroundings (identical or connected with usual thermodynamic baths) with mutual strong correlations (entanglement), the standard statistical thermodynamics could be violated. This is in particular, but not only, the case of the second law of thermodynamics. One must keep in mind that from first principles (microscopic Hamiltonian dynamics), derivations the second law are declared to exist just in classical (in the sense of non-quantum) physics [14] or, as in standard textbooks, involving assumption of a weak system-bath coupling only. [1] It should be stressed already here that the classical physics is, according to the Bohr correspondence principle, an infinite temperature limit of the (more general) quantum physics. This, inter alia, implies that its application to finite temperatures as in standard thermodynamics is at least open to discussion. The above lack of general derivation of the second law beyond the classical regime could also correspond to the fact that so far reported and seemingly classical paradoxes connected with the second law (see, e.g., [15]) usually involve sufficiently intense processes that are inherently of the quantum character.

[1] Gibbs canonical form of the system density matrix compatible with the standard thermodynamics is correct to just the zeroth order in the system-bath coupling. This is an important fact to be realized already here as the effect reported below is of higher order in this coupling.

In 1999, it was realized that a long lasting call in chemistry for inclusion of self-organizational tendencies into theory of particle-transfer chemical reactions is, from the microscopic point of view, nothing but a call for inclusion of such mechanisms that can turn any (from the thermodynamical point of view) passive bath into an active one, opening thus door to violations of standard thermodynamic principles [16]. Recent review of theoretical models and state-of-art in theory could be found in, e.g., [17, 18]. So far, two main groups of theoretical models of purely quantum open systems violating the second law existed: Those with quantum reaction channels opening or closing in accordance with the instantaneous state of the system (reminding of the Maxwell demon [3] closing and opening gate in a wall separating two compartments with a classical gas), and those where a specific type of interference of different quantum reaction channels exists [17]. In particular this type of systems is relevant as the contradiction with the second law treated in [17] is not only mathematically well justified but can be given even a very simple physical interpretation based on otherwise experimentally well established facts: This is the on-energy-shell (i.e. induced by elastic transfer mechanisms) diffusion of excitons among tails of exciton local levels broadened by finite-life-time effects. This diffusion goes, as it is always the case of diffusion in experiment, prevailingly to exciton sites with lower exciton population that may be due to higher exciton excitation energy. Thus, the exciton flow bearing energy can go even against moderate temperature steps preserving such a population inequality between (among) exciton localized states (sites).

Recently, as a theoretical response to another positively tested experimental system [11], a next model of still another type has been suggested [19] that also allows rigorous solution (exact within a scaling theory) fully confirming experimental doubts about universal validity of the second law. Detailed discussion and solution of a modified (and nearer to reality) version of the model is the subject of the present paper. What is perhaps universal for all the models challenging thermodynamics is that the system in question must be, during its activity, outside the canonical state. Mechanisms how to achieve and maintain that might be, of course, different. One should understand, however, that this condition is perhaps necessary but by far not sufficient. For other paradoxical systems that could be also classified as above, showing how physics beyond the second law is still little understood see, e.g., [15, 20].

II. THEORETICAL MODEL

We should like to stress that we shall, except for model assumptions, use no approximate steps in our reasoning. This will certainly make position of our potential opponents more difficult. Moreover, mathematics we are going to use in the main text is that one by Davies [24, 25] which then forms, for one specific choice of the scaling parameter, mathematical basis of the weak-coupling kinetic relaxation theory confirming, for the weak-coupling limit, validity of the second law. (Another possibility of deriving basic kinetic equations (11) below may be connected with the Tokuyama - Mori identity stemming from the Heisenberg equations of motion for quantum operators - see, for another model, e.g. [18].) We fully rely upon the Davies mathematics and use, for the chosen model (i.e. a specific case) no additional approximations. Hence, rigour of our approach below is that one of the general Davies theory. We only deviate from a subsequent standard application of general Davies theorems to the weak coupling situation by just another, but equally admissable and physically motivated, choice of the scaling parameter. This choice makes the theory physically applicable also beyond the weak coupling limit. In the Appendix, we shall even avoid scaling arguments at all. In both cases, as we have numerically verified and as it is also argued below, our results well coincide with those of the weak-coupling theories in the overlap region with the weak-coupling regime. We thus have no doubts on the validity of the second law there. However, beyond the weak coupling regime, our results become appreciably different from standard ones. Physically, we have reasons supported by arguments to understand that: This is a deviation from the canonical state of the system caused by its non-negligible coupling to the bath. As far as the underlying Davies mathematics is concerned, it is general (valid for any choice of the scaling parameter) and cannot be consequently sometimes correct and sometimes not. It can be either correct or not in general; no other alternative exists. The first alternative provides solid basis for arguments in favour of correctness of our approach while the second one (that was even never suggested or indicated) deprives even the weak coupling relaxation theory of its mathematical foundation. Rejecting these alternatives would

- either mean to question physical as well as mathematical principles (including the Liouville equation) on which all the existing renown of description of kinetic phenomena via corresponding kinetic equations (depending on the regime in question) relies,

- or to admit that the very principles of quantum mechanics of the open system would have to be complemented by, e.g., some additional requirements not admitting models of the type investigated here.

In view of existing experimental evidence in favour of the quantum theory as well as because of experimental results indicating violations of the second law in experiment [11, 21, 22, 23], both the latter possibilities seem, in our opinion, rather unlikely. In any case, the conclusions suggest that there is at least something in physics beyond the second law what is at present still insufficiently understood.

Our system, in accordance with the experimental system [11], is assumed to consist of three sites, designated as 1, 2, and 3. The reader is referred to [11] or [19] if he/she is interested in the motivation for construction of the model. The latter is, as compared to [19], only slightly modified here so that it now better corresponds to the experimental system of [11]. Shortly, the above sites correspond to walls of the plasma container, plasma, and the probe. Hamiltonian of the system reads

$$H_S = \sum_{j=2}^{3} \epsilon_j a_j^\dagger a_j + J(a_1^\dagger a_2 + a_2^\dagger a_1) + K(a_2^\dagger a_3 + a_3^\dagger a_2), \tag{1}$$

where the zero of the energy is taken to be at the walls (site 1). Though it is not in principle important, we assume here $\epsilon_3 > \epsilon_2 > 0$. We assume only one electron in the system that is elastically transferred between sites 1 and 2, and simultaneously between sites 2 and 3. This is in accordance with, e.g., the standard theory of the Richardson-Dushman thermal emission (for the 1 - 2, i.e. wall - plasma transfers) that is based on the idea of prevailingly elastic transfer upon, e.g., electron leaving surface of solids.

The load between the probe and walls in the Sheehan's experimental set-up [11] is the location at which the electron can inelastically scatter. This means, in our case, phonon-assisted $3 \leftrightarrow 1$ transitions. The phonons involved are assumed to be those of the load, here designated as bath II. In addition to that, we assume another bath, say bath I, formed by phonons (physically, those from the walls) interacting site-locally with the electron located on site 1. This means that Hamiltonian H_B of the bath of our model reads as

$$H_B = H_B^I + H_B^{II},$$

$$H_B^I = \sum_\kappa \hbar\omega_\kappa b_\kappa^\dagger b_\kappa, \quad H_B^{II} = \sum_\kappa \hbar\omega_\kappa B_\kappa^\dagger B_\kappa. \tag{2}$$

The electron-bath coupling, H_{S-B}, is given by

$$H_{S-B} = H^I_{S-B} + H^{II}_{S-B},$$

$$H^I_{S-B} = \frac{1}{N} \sum_{\kappa_1 \neq \kappa_2} \hbar \sqrt{\omega_{\kappa_1} \omega_{\kappa_1}} g_{\kappa_1,\kappa_2} a_1^\dagger a_1 (b_{\kappa_1} + b_{\kappa_1}^\dagger)(b_{\kappa_2} + b_{\kappa_2}^\dagger),$$

$$H^{II}_{S-B} = \frac{1}{\sqrt{N}} \sum_{\kappa} \hbar \omega_\kappa G_\kappa (a_3^\dagger a_1 + a_1^\dagger a_3)(b_\kappa + b_\kappa^\dagger). \qquad (3)$$

(Contingent terms with $\kappa_1 = \kappa_2$ in H^I_{S-B} could be turned below to just a temperature-dependent renormalization of site-energy ϵ_1 of site 1 that we set zero here.) Here the anti- or commutational relations between creation and annihilation operators for electrons and phonons are as usual. Also N designates the number of phonon modes; here it is understood that $N \to +\infty$. Notice that H^I_{S-B} is quadratic in the phonon operators; this is certainly admissable but contrasts with both tradition and the treatment of phonon operators in H^{II}_{S-B}. This non-standard assumption is employed to preserve the finite dephasing and local electron heating after the Davies scaling procedure (preserving formally just the lowest-order effects in the scaling parameter) which now follows. Otherwise, we would have to involve higher-order effects in treating the dephasing what could make the theory and the final statements, in eyes of a sceptic reader, rather ambiguous. In any case, we have a freedom to choose the model as above. Concerning H^I_{S-B}, one should also notice that the on-site dephasing is here, in contrast to the model from [19], on site 1. This corresponds, in the experimentally tested system of [11], to electron heating inside the walls of the plasma container.

One should first of all realize that the phonon-assisted transfers $3 \leftrightarrow 1$ as provided by H^{II}_{S-B} enable the electron to move in a circle $1 \to 2 \to 3 \to 1$, or *vice versa* $1 \leftarrow 2 \leftarrow 3 \leftarrow 1$. These two circular motions cannot, however, compensate each other. This is the first of two basic physical observations on which the present model relies. The point is that all the inter-site transfers involved are elastic, i.e. symmetric, except for the $3 \leftrightarrow 1$ one. Such elastic transfers lead to a tendency of equilibration of site occupation probabilities. For instance, assume for a while that we had only a dimer composed of sites 1 and 2, with the coherent (i.e. elastic) hopping term $J(a_1^\dagger a_2 + a_2^\dagger a_1)$ decoupled from any bath. The Hamiltonian reads then $H_S = \epsilon_2^\dagger a_2 + J(a_1^\dagger a_2 + H.C.)$ as above. Stationarity of the solution we are interested in implies $\rho_{12} = \rho_{21}$. Contingently nonzero values of these site-off-diagonal elements are connected with a 1-2 bonding. If we add a mechanism breaking such bonds (but,

for simplicity, causing no additional $1 \leftrightarrow 2$ transfer), magnitude of $\rho_{12} = \rho_{21}$ would become suppressed below their maximum value given by positive semi-definiteness of ρ. Concerning the site-diagonal elements ρ_{jj}, their stationary values can be investigated by generalized master equations where memory functions determine the $1 \leftrightarrow 2$ balance. These memory functions (and also their time integrals whose ratio determines $\rho_{11}(+\infty)/\rho_{22}(+\infty)$) contain two channels [26], sometimes interpreted as phonon- (or bath-) assisted and quasicoherent one [27]. The latter channel is, in contrast to the former one, symmetric what is the reason of generally comparable stationary values of $\rho_{11}(+\infty)$ and $\rho_{22}(+\infty)$. Full equilibration $\rho_{11}(+\infty) = \rho_{22}(+\infty)$ then follows from our mathematics below upon full ignoring site 3, as a consequence of elastic character of the $1 \leftrightarrow 2$ transitions. The same applies for dimer 2 and 3 once it is separated from the rest of the system. These facts will be useful below. With that, it is then easy to show that the equality of populations $\rho_{11} = \rho_{33}$ stemming from above reasoning based on the elastic character of the J- and K-induced elastic transfers cannot comply with equilibration of the inelastic phonon-assisted transitions $3 \leftrightarrow 1$ leading $\rho_{11} > \rho_{33}$ or possibly even to $\rho_{11} \gg \rho_{33}$. This fact will be useful to understand the results obtained below. A word of warning is, however, worth already here: What is here now being explained are still just heuristic arguments supported by previous investigations that explain our motivation; true rigorous mathematics comes only below. As it follows from general arguments above as well as the mathematics of the next sections, we do understand why, e.g., the detailed balance conditions could in our system become violated. This is because these conditions do not apply to uphill or downhill transfers caused by elastic mechanisms. We, however, do not raise the question about violations or preserving these conditions here. Our rigorous mathematics below avoids such statements and formulations, and leads directly to the required results and effects investigated here.

For that, let us return to our model (1-3). Between sites 1 and 3, there is an imbalance mechanism owing to spontaneous processes allowed by H^{II}_{S-B} that prefers, because of assumed $\epsilon_3 > 0$, the $3 \to 1$ transitions to $1 \to 3$ ones. This is the imbalance (and the only imbalance existing in our system) that makes domination of the circular motion $1 \to 2 \to 3 \to 1$ over the $1 \leftarrow 2 \leftarrow 3 \leftarrow 1$ one in fact possible. Owing to the phonon-assisted (prevailingly down-hill, i.e. $3 \to 1$) character of the $3 \leftrightarrow 1$ transfer, this implies heat transfer to bath II. (Each transfer act $3 \to 1$ is connected, because of the energy conservation law, with emission of a phonon quantum into bath II. Similarly for the back transfer $3 \leftarrow 1$ and

phonon absorption. If the former transfers prevail, we get the net heat flow to bath II.) The question is, however, where this heat could come from. The only possible answer is that it is from bath I. Really, dephasing at site 1 means nothing but a continuous emission and absorption of phonons from bath I that can provide the necessary energy transferred by the electron whose energy is not sharp. Simultaneously, this dephasing can break phase relations between amplitude of finding the electron at site 1 and those elsewhere, i.e. it breaks the corresponding covalent-type of bonds. Without the sufficiently strong dephasing, the electron distribution in the system (as prescribed by, e.g., the canonical density matrix to which the density matrix usually tends within weak-coupling theories considering coupling to bath as infinitesimally weak) would really contain such *and fully developed* J- and K-induced bonds. Thus, it would be stiff enough in the respect that irrespective of the above imbalance, no electron circular motion would finally appear. One can easily verify that by calculating, e.g., the electron flow between any two sites. We always get (by the way, in a correspondence with standard physical reasoning) zero mean flow in the canonical (i.e. zeroth-order in the coupling to the bath) state of the system. From this point of view, lack of on-site amplitude dephasing (or, in other words, that of partial violations of such covalent bonds re-appearing immediately once the system coupling to the bath is re-introduced as a source of corrections to the canonical form of its density matrix) is one of the greatest deficiencies of the weak-coupling kinetic approaches leading to such canonical distributions. For illustration, notice that site off-diagonal elements of the density matrix become, in the weak-coupling kinetic theories, asymptotically independent of the strength of the site-local coupling to the bath even when this type of the coupling causes bath-induced (and on different sites uncorrelated) fluctuations of site energies (see, e.g., formula (28) of [28]). So, even when the model does describe it, its weak-coupling kinetic relaxation formalism is in principle unable to describe the dephasing and breaking of the bonds. Hence, in our case here, we must definitely go beyond the weak coupling kinetic theory in especially the dephasing rate at site 1. This is the second basic and, perhaps, the most important observation connected with the model and the effect we should like to describe here. (One could also pose a question why we should be so keen to describe and include such potentially weak corrections to, e.g. violations of covalent $1-2$ and $2-3$ bonds here. The point is that these violations provide perhaps just small corrections to the canonical density matrix of the system but, simultaneously, these corrections are the very source of the effect we are

interested in.) One should add that in our approach involving other than the weak coupling scaling below, we also take the limit of the infinitesimal coupling to bath, i.e. infinitesimal dephasing. On the other hand, we simultaneously scale also the hopping (transfer) integrals what makes the ratio of the in-phasing and dephasing constant. This, in contract to the standard weak coupling scaling, corresponds to reality and allows the above bond breaking. Thus we have a hope, and really do obtain below the effect expected. So far, of course, all these ideas provide us with at most a physical background of the model, its mathematical treatment, and physics beyond. So, let us now have a look at how these ideas work within a rigorous theory.

III. DAVIES SCALING AND KINETIC EQUATIONS

The scaling procedure we use is based on Davies [24, 25]. (Another type of arguments, which is fully non-scaling though it is technically tightly connected with our scaling approach here, may be found in the Appendix.) We, however, extend our treatment beyond standard weak coupling theory in that we scale not only time and H_{S-B}, but also the transfer (overlap, hopping, or resonance) integrals J and K, setting [29]

$$t = t'/\lambda^2, \quad H_{S-B} \propto \lambda, \quad J \propto \lambda^2, \quad K \propto \lambda^2 \tag{4}$$

(t' playing the role of a new rescaled time.) As usual, we then project off the bath and let $\lambda \to 0$. Such a physical regime where intersite hopping (transfer) integrals determining rates of bath-free transfers inside system get comparable with rates of bath-assisted processes (transfers) can be definitely *not* that of the weak coupling but rather that of the intermediate or, in a sense, even contingently strong coupling to the bath. Technically, though the mathematics used is completely that by Davies [24], we proceed simultaneously according to [29] where the relevant formulae are rewritten in a physically understandable form.

The Davies formalism starts by writing total Hamiltonian

$$H = H_S + H_B + H_{S-B} \tag{5}$$

in form

$$H = H_0 + \lambda H_1. \tag{6}$$

Here, one should add that $\lambda H_1 \propto \lambda$ but that does not exclude the possibility that λH_1 includes also higher orders in λ (λ^2 if (4) is accepted). Those who do not like this way of

thinking could replace conditions $J \propto \lambda^2$, $K \propto \lambda^2$ in (4) by $J \propto \lambda$, $K \propto \lambda$ and proceed as below. The final result is the same.

Next, introduce superoperators $\mathcal{L}_0 = \frac{1}{\hbar}[H_0, \ldots]$ and $\mathcal{L}_1 = \frac{1}{\hbar}[\lambda H_1, \ldots] \propto \lambda$. Finally, be

$$\mathcal{P} \ldots = \rho^B \otimes \mathrm{Tr}_B(\ldots) \tag{7}$$

(with $\mathrm{Tr}_B \rho^B = 1$ implying $\mathcal{P}^2 = \mathcal{P}$) the Argyres-Kelley projector (projection superoperator) in the Liouville space of operators that act in the Hilbert space of the system and bath. Then the message of Davies (see Eq. (1.19) of [24] or Eq. (14) of [29]) is

$$\lim_{\lambda \to 0} \sup_{0 \leq \lambda^2 t \leq a} ||\rho(t) - \mathrm{e}^{-i(\mathcal{L}_0 + \langle \mathcal{L}_1 \rangle + i\lambda^2 \mathcal{K})t} \rho(0)|| = 0,$$

$$\lambda^2 \mathcal{K} \ldots = \int_0^{+\infty} dx \, Tr_B \, (\mathrm{e}^{i\mathcal{L}_0 x}(-i\mathcal{L}_1)\mathrm{e}^{-i\mathcal{L}_0 x}(1-\mathcal{P})(-i\mathcal{L}_1)(\rho^B \otimes \ldots),$$

$$\langle \mathcal{L}_1 \rangle \ldots = Tr_B(\rho^B \otimes \mathcal{L}_1 \ldots). \tag{8}$$

(Finite constant a is here arbitrary.) Here $\rho(t) = \mathrm{Tr}_B \rho^{S+B}(t)$ is the density matrix of the complex 'system + bath' with its time-development determined from the exact Liouville equation $i\frac{d}{dt}\rho^{S+B}(t) = (\mathcal{L}_0 + \mathcal{L}_1)\rho^{S+B}(t)$. The assumptions used were

- that the density matrix of the system and bath $\rho^{S+B}(t)$ is initially separable, i.e. that

$$\rho^{S+B}(0) = \rho^B \otimes \rho(0), \tag{9}$$

  and

- that $\mathcal{P}\mathcal{L}_0 = \mathcal{L}_0\mathcal{P}$. This condition can be, however, well fulfilled as far as, e.g., $\rho^B = f(H_B^I, H_B^{II})$, $[H_B^I, H_B^{II}] = 0$. This is in particular in our case because we are forced to assume

$$\rho^B = \frac{\exp(-\beta_I H_B^I - \beta_{II} H_B^{II})}{\mathrm{Tr}_B \exp(-\beta_I H_B^I - \beta_{II} H_B^{II})} \tag{10}$$

  to be able to introduce properly the initial temperatures of baths I and II separately.

Meaning of the mathematically exact statement in the first row of (8) is that time development of $\rho(t)$ as prescribed by the exact Liouville equation for the density matrix $\rho^{S+B}(t)$ of the complex 'system + bath' is not discernable, in the scaling limit $\lambda \to 0$, from that one dictated by the kinetic equation for the density matrix $\rho(t)$ of just the system

$$i\frac{d}{dt}\rho(t) = (\mathcal{L}_0 + \langle \mathcal{L}_1 \rangle + i\lambda^2 \mathcal{K})\rho(t). \tag{11}$$

This general and exact result should now be specified according to the choice of H_0 and λH_1 in (6).

Two main possibilities exist.

- Either we accept so called weak-coupling scaling according to van Hove (and often automatically accepted in general situations)

$$t = t'/\lambda^2, \quad H_{S-B} \propto \lambda, \quad J = \text{const}, \quad K = \text{const} \tag{12}$$

(again with $\lambda \to 0$) which would correspond to the choice

$$H_0 = H_S + H_B, \quad \lambda H_1 = H_{S-B}. \tag{13}$$

Then $\lambda^2\mathcal{K}$ in (11) is nothing but the weak-coupling relaxation superoperator and (11) reduces to the Redfield equation (before using the Redfield secular approximation) [30, 31, 32]. The relaxation is then to the canonical state of the system.

- Or we assume (4) what means to identify

$$H_0 = H_S|_{J=K=0} + H_B, \quad \lambda H_1 = H_{S-B} + H_S|_{J\neq 0,\, K\neq 0} - H_S|_{J=K=0}. \tag{14}$$

Then several things have to be realized:

  - Though the relaxation superoperator $\lambda^2\mathcal{K}$ in (11) [as defined in (8)] involves formally also higher orders in λ, application of the rule $\mathrm{Tr}_B([a_m^\dagger a_n, \ldots]) = [a_m^\dagger a_n, \mathrm{Tr}_B(\ldots)]$ yields that in fact just second order terms in λ survive.
  - Because now $\mathcal{L}_0 = \frac{1}{\hbar}[H_S|_{J=K=0} + H_B, \ldots]$ and $H_S|_{J=K=0}$ is site-diagonal, the relaxation is *not any more* (like in case of the weak-coupling choice (13)) among eigenstates of H_S but, instead, among those (site-local eigenstates) of $H_S|_{J=K=0}$. On the other hand, in (11), terms $\mathcal{L}_0 + \langle\mathcal{L}_1\rangle$ reproduce $\frac{1}{\hbar}[H_S, \ldots] \equiv \frac{1}{\hbar}[H_S|_{J\neq 0\neq K}, \ldots]$ what is a free propagation among eigenstates of the full (site-off-diagonal) H_S. This competition between site-local and site off-local tendencies of the time development is what makes the dynamics much richer than in the weak-coupling case.
  - The fact that $\lambda^2\mathcal{K}$ describes relaxation in the site-local basis is *not* owing to neglecting anything or any type of approximation. It is owing to choice of another regime; in our case that one in which J- and K-induced processes become at most comparable with those caused by the system interaction with the bath.

Those who anyway do not like our identification (14) could start from (8) with the standard identification (13) and invoke then the identity

$$\lim_{\lambda\to 0}\sup_{0\leq\lambda^2 t\leq a}||\mathrm{e}^{-i(\mathcal{L}_0+\langle\mathcal{L}_1\rangle+i\lambda^2\mathcal{K})t}\rho(0)-\mathrm{e}^{-i(\mathcal{L}_0+\langle\mathcal{L}_1\rangle+i\lambda^2\mathcal{K}|_{J=K=0})t}\rho(0)||=0 \qquad (15)$$

that is based on the assumption that both J and K are $\propto\lambda^2$. The observation that $\lambda^2\mathcal{K}|_{J=K=0}$ is then nothing but the relaxation superoperator as obtained from our choice (14) again implies that

- (11) with the relaxation superoperator yielding relaxation among site-local eigenstates of $H_S|_{J=K=0}$ is a proper choice for describing time-develoment of $\rho(t)$ in the regime where the bath-induced processes in the system are at least comparable with those inside the system alone (J- and K-induced particle transfer), and
- that this choice of the relaxation superoperator cannot be questioned on grounds of formal objections against our (physically motivated) choice (14).

This all justifies our choice of (non-Redfield) form of $\lambda^2\mathcal{K}$ relaxation superoperator yielding relaxation among site-local states. On the other hand, identity (15) may be also formally viewed as a reconciliation of two different scalings that give, in the extreme limit of zero scaling parameter λ, identical results. In other words, as if we were trying to say '...does not matter which form of the relaxation tensor, site-local or non-local, we take...'. This statement is, however, not true. The situation reminds that of the Redfield theory without and with the Redfield secular approximation [30, 31]. Both these approaches correspond to the standard choice (13) but with two different Davies forms of the relaxation tensor (Theorem 1.2 of [24] as compared with the second form in Theorems 2.1 and 2.2 of [33]). Theorem 1.4 of [24] establishes what is considered to be a full and complete equivalence of the theory without and with the Redfield secular approximation (compare discussion in [29]). This equivalence means, however, just equivalence in the strict and complete $\lambda\to 0$ limit. It is, on the other hand, known that all coupling constants are in physics finite and it is also correspondingly well known and established that for any finite value of λ, the two schemes (without and with the Redfield secular approximation) differ (with increasing λ even) appreciably [34, 35]. So physics must always be in such (mathematically unresolved) situations taken into account. (The problem is not in an impossibility to solve the mathematically well posed problem, but in the fact that mathematics gives answer regarding just the $\lambda\to 0$

limit while physics concerns the situations where λ remains finite.) Here, concerning the schemes with the site-local and site non-local forms of the relaxation superoperator, we use formally the same general form of the relaxation superoperator (tensor) (corresponding to Theorem 1.2 of [24]) but use another (than usual) scaling scheme (not (13) but rather (4)). Equation (15) implies that *in the strict* $\lambda \to 0$ *limit* and finite interval of times t', it does not matter which way, i.e. site-local or off-local form of the relaxation superoperator we use. However, we again know that all coupling constants in Nature are finite. That is why *for finite* λ, the two schemes may differ even appreciably. So, again as with the problem of correspondence between Redfield schemes without and with the Redfield secular approximation, rather physical arguments should be invoked. Additional and, in our opinion, the decisive mathematical argument can be found in the Appendix.

The physical argument in favour of the form of the relaxation superoperator corresponding to the choice (14) is that we are interested in the regime in which the bath-assisted processes inside the system are at least comparable with, or even dominating over the internal transfer processes inside the system caused, in our case, by the J- and K-dependent hopping terms in H_S (1). Once we realize that the weak-coupling theory *presumes*, in the sense of (12), the system-bath coupling to be infinitesimal, i.e. infinitely times weaker than all other relevant competing transfer and relaxation mechanisms, this excludes scaling (12), i.e. the choice (13), in the regime considered here. On the other hand, it allows to use (4), i.e. the choice (14). That is why we shall below stick to this alternative. So, we use $\mathcal{K}$ from (8) with (14) for our model (1-3). This means the Redfield form of $\mathcal{K}$ in the localized basis as a consequence of another (than the weak-coupling) physical regime, i.e. also correspondingly another form of identification of perturbation. So, this form of the Redfield tensor is definitely *not* any consequence of any additional approximation applied to the Redfield form of the relaxation superoperator in the weak-coupling regime (for discussion of such an approximation in the weak-coupling regime see [36]). After some straightforward algebra, (11) then turns in the

site representation to

$$i\hbar\frac{d\rho}{dt} \equiv i\hbar\frac{d}{dt}\begin{pmatrix}\rho_{11}\\ \rho_{22}\\ \rho_{33}\\ \rho_{12}\\ \rho_{21}\\ \rho_{13}\\ \rho_{31}\\ \rho_{23}\\ \rho_{32}\end{pmatrix} = \begin{pmatrix} & \cdot & \\ & \cdot & \\ \mathcal{A} & \cdot & \mathcal{B} \\ & \cdot & \\ & \cdot & \\ & \cdot & \\ & \cdot & \\ \mathcal{B}^T & \cdot & \mathcal{C} \\ & \cdot & \end{pmatrix} \cdot \begin{pmatrix}\rho_{11}\\ \rho_{22}\\ \rho_{33}\\ \rho_{12}\\ \rho_{21}\\ \rho_{13}\\ \rho_{31}\\ \rho_{23}\\ \rho_{32}\end{pmatrix} . \tag{16}$$

The sub-matrices $\mathcal{A}$, $\mathcal{B}, \mathcal{C}$ ($\mathcal{B}^T$ is the transpose of $\mathcal{B}$) are given as

$$\mathcal{A} = \begin{pmatrix} -i\hbar\Gamma_\uparrow & 0 & i\hbar\Gamma_\downarrow & -J & J \\ 0 & 0 & 0 & J & -J \\ i\hbar\Gamma_\uparrow & 0 & -i\hbar\Gamma_\downarrow & 0 & 0 \\ -J & J & 0 & -2i\hbar\Gamma - \frac{i\hbar}{2}\Gamma_\uparrow - \epsilon_2 & 0 \\ J & -J & 0 & 0 & -2i\hbar\Gamma - \frac{i\hbar}{2}\Gamma_\uparrow + \epsilon_2 \end{pmatrix},$$

$$\mathcal{B} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -K & K \\ 0 & 0 & K & -K \\ -K & 0 & 0 & 0 \\ 0 & K & 0 & 0 \end{pmatrix},$$

$$\mathcal{C} = \begin{pmatrix} -2i\hbar\Gamma - \frac{i\hbar}{2}(\Gamma_\uparrow + \Gamma_\downarrow) - \epsilon_3 & \frac{i\hbar}{2}(\Gamma_\uparrow + \Gamma_\downarrow) & J & 0 \\ \frac{i\hbar}{2}(\Gamma_\uparrow + \Gamma_\downarrow) & -2i\hbar\Gamma - \frac{i\hbar}{2}(\Gamma_\uparrow + \Gamma_\downarrow) + \epsilon_3 & 0 & -J \\ J & 0 & -\frac{i\hbar}{2}\Gamma_\downarrow + \epsilon_2 - \epsilon_3 & 0 \\ 0 & -J & 0 & -\frac{i\hbar}{2}\Gamma_\downarrow - \epsilon_2 + \epsilon_3 \end{pmatrix}. \tag{17}$$

Here, we have used the notation

$$\Gamma_\uparrow = \frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa |\hbar\omega_\kappa|^2 |g_\kappa|^2 n_B(\beta_{II}, \hbar\omega_\kappa)\delta(\hbar\omega_\kappa - \epsilon_3),$$

$$\Gamma_\downarrow \equiv \frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa |\hbar\omega_\kappa|^2|g_\kappa|^2[1+n_B(\beta_{II},\hbar\omega_\kappa)]\delta(\hbar\omega_\kappa-\epsilon_3)=\Gamma_\uparrow\cdot \mathrm{e}^{\beta_{II}\epsilon_3},$$

$$2\Gamma = \frac{2\pi}{\hbar}\frac{1}{N^2}\sum_{\kappa_1,\kappa_2} |g_{\kappa_1,\kappa_2}|^2(\hbar\omega_{\kappa_1}\omega_{\kappa_2})^2 n_B(\beta_I,\hbar\omega_{\kappa_1})[1+n_B(\beta_I,\hbar\omega_{\kappa_2})]\delta(\hbar\omega_{\kappa_1}-\hbar\omega_{\kappa_2}),$$

$$n_B(\beta,z)=\frac{1}{\mathrm{e}^{\beta z}-1}, \tag{18}$$

where $T_{I(II)} = 1/(k_B\beta_{I(II)})$ are the initial temperatures of Baths I and II; $n_B(\beta,z)$ is the Bose-Einstein phonon distribution function. $\Gamma_\uparrow$ and $\Gamma_\downarrow$ are the Golden Rule formulae for transfer rates $1 \to 3$ and $3 \to 1$. Note that $\Gamma_\uparrow$ and $\Gamma_\downarrow$ are different solely in that the latter involves a $1+n_B$ term, whereas the former has only n_B. Physically, this corresponds to $\Gamma_\uparrow$ involving only bath-assisted stimulated up-hill transitions (absorption), whereas $\Gamma_\downarrow$ involves both bath-assisted spontaneous and bath-assisted stimulated down-hill transitions (emission). Finally, 2Γ determines the rate of dephasing arising from local electron-energy fluctuations from Bath I, and also the rate of electron heating in the walls (site 1).

A few comments are worth mentioning already here. First, notice that temperature T_I of bath I enters (16) only via the dephasing (and simultaneously heating) rate 2Γ. This rate depends, however, also on strength and details of the electron coupling to bath I. Thus, moderate changes of T_I may be well compensated by those of the coupling and *vice versa*. As there are no abrupt qualitative changes expected with moderate changes of the coupling, only continuous changes of, e.g., the electron $1 \to 2 \to 3$ flow are expected when (the initial) temperature T_I of bath I sinks below that (i.e. T_{II}) of bath II. This is important for interpretation of the result to be obtained below. Finally, concerning (the initial) temperature T_{II} of bath II: We shall assume here the inequality

$$k_B T_{II} \lesssim \epsilon_3. \tag{19}$$

The opposite inequality would imply high-temperature regime in which the spontaneous $3 \to 1$ processes would become negligible with respect to stimulated ones. So, asymptotically, $\Gamma_\uparrow/\Gamma_\downarrow$ would turn to unity and the driving force in the circle $1 \to 2 \to 3 \to 1$ would disappear implying disappearance of the electron flow. This means that also the contradiction with the second law we aim at would disappear, in a full correspondence with the Bohr correspondence principle and the Martynov proof of validity of the second law in classical statistical mechanics [14]. On the other hand, the low-temperature limitation (19) is not severe. With, e.g., $\epsilon_3 \approx 1$eV, temperatures T_{II} appreciably higher than room temperatures are viable.

IV. ANALYTICAL SOLUTION AND STEADY-STATE HEAT-FLOW

Let us henceforth investigate the stationary situation. Then the left hand side of (16) equals zero so that we have a homogeneous set of 9 linear algebraic equations for the stationary values of the electron density matrix. The matrix rank is, however, only 8 since the sum of its first three rows is zero. Thus, the set can (and must) be complemented by the normalization condition

$$\rho_{11} + \rho_{22} + \rho_{33} = 1. \tag{20}$$

This provides us with a complete inhomogeneous set of 9 linear algebraic equations for 9 elements of the particle density matrix. The site-diagonal matrix elements ρ_{jj} give the probabilities of finding the electron at site j. Full algebraic solution of this set of equations is possible but unwieldy. That is why the set will be solved numerically below. First, however, we shall analytically prove that there is always, for nonzero temperatures T_I and T_{II}, a positive electron flow $1 \to 2 \to 3 \to 1$ implying, for $T_I < T_{II}$, violation of the second law of thermodynamics in its Clausius formulation. The proof is made by logical contradiction. We stress from the outset that the mathematical derivation of our starting equations (16), including scaling, involves no approximation; therefore, aside from the model assumptions, our treatment here is fully rigorous, in the full mathematical meaning of the word.

Cyclic mean electron flow in the system (taken as positive in the direction $1 \to 2 \to 3 \to 1$) can be written, on grounds of physical meaning of $\Gamma_\uparrow$ and $\Gamma_\downarrow$ in (18), as

$$\mathcal{J} = \Gamma_\downarrow \rho_{33} - \Gamma_\uparrow \rho_{11}. \tag{21}$$

From the first and second equations of (16) one also has

$$\mathcal{J} = \frac{i}{\hbar} J(\rho_{21} - \rho_{12}) = \frac{i}{\hbar} K(\rho_{32} - \rho_{23}). \tag{22}$$

These formulae can be also easily derived from elementary quantum mechanics. Assume now that no heat flows directly from bath I to bath II and *vice versa*. So, only the electron-mediated heat flow from I to II may appear. Since the $3 \leftrightarrow 1$ phonon-assisted transitions are associated with influx or efflux of energy (heat) to or from Bath II (proportionally to the magnitude of ϵ_3), the total mean heat flow from Bath I to Bath II may be written as

$$\mathcal{Q} = \epsilon_3 \mathcal{J}. \tag{23}$$

This is the main quantity we are interested in.

Let as now *assume*, in accord with our strategy of proof by contradiction, that there is no heat flow between the baths, i.e.

$$\mathcal{Q} = 0. \tag{24}$$

Since $\epsilon_3 > 0$, this implies, via (21) and (23), that

$$\Gamma_\downarrow \rho_{33} - \Gamma_\uparrow \rho_{11} = 0. \tag{25}$$

The reader could easily recognize that (25) is nothing but a detailed balance condition for inelastic phonon-assisted $1 \leftrightarrow 3$ direct transitions. Because of (22) this also implies that

$$\rho_{21} = \rho_{12}, \quad \rho_{32} = \rho_{23}. \tag{26}$$

Now, summing the forth and fifth equations of (16) with zero left hand side, we get

$$0 = \frac{K}{\hbar}(\rho_{31} - \rho_{13}) + (-2i\Gamma - \frac{i}{2}\Gamma_\uparrow)(\rho_{12} + \rho_{21}) + \frac{\epsilon_2}{\hbar}(\rho_{21} - \rho_{12}). \tag{27}$$

Similarly, from the sixth and seventh equation, and also from the eighth and ninth equation of (16) (always with zero left hand side), we get

$$0 = \frac{K}{\hbar}(\rho_{21} - \rho_{12}) - 2i\Gamma(\rho_{13} + \rho_{31}) + \frac{\epsilon_3}{\hbar}(\rho_{31} - \rho_{13}) + \frac{J}{\hbar}(\rho_{23} - \rho_{32}) \tag{28}$$

and

$$0 = \frac{J}{\hbar}(\rho_{13} - \rho_{31}) + \frac{\epsilon_2 - \epsilon_3}{\hbar}(\rho_{23} - \rho_{32}) - \frac{i}{2}\Gamma_\downarrow(\rho_{23} + \rho_{32}). \tag{29}$$

In combination with (26), Eqs. (27-29) give

$$\rho_{12} = \rho_{21} = \frac{K/\hbar}{2\Gamma + \frac{1}{2}\Gamma_\uparrow} \Im\mathrm{m}\ \rho_{31}, \tag{30}$$

$$\Re\mathrm{e}\ \rho_{31} = \frac{\epsilon_3}{2\hbar\Gamma} \Im\mathrm{m}\ \rho_{31}, \tag{31}$$

and

$$\rho_{23} = \rho_{32} = -\frac{2J}{\hbar\Gamma_\downarrow} \Im\mathrm{m}\ \rho_{31}. \tag{32}$$

Let us now take difference of the fourth and sixth equation in (16) in the stationary state. Owing to (30-31), it gives

$$0 = -\frac{J}{\hbar}(\rho_{11} - \rho_{22}) + \left\{ -\frac{\epsilon_2}{\hbar} \frac{2K/\hbar}{2\Gamma + \frac{1}{2}\Gamma_\uparrow} - \frac{K}{\hbar} \frac{\epsilon_3}{\hbar\Gamma} \right\} \Im\mathrm{m}\ \rho_{31}. \tag{33}$$

Similarly, from the difference of the sixth and seventh equation and taking into account (27), (31) and (32), we obtain

$$0 = \left[(\frac{K}{\hbar})^2 \frac{1}{\Gamma + \frac{1}{4}\Gamma_\uparrow} + (\frac{J}{\hbar})^2 \frac{4}{\Gamma_\downarrow} + (\frac{\epsilon_3}{\hbar})^2 \frac{1}{\Gamma} + 2(2\Gamma + \Gamma_\uparrow + \Gamma_\downarrow) \right] \Im\mathrm{m}\ \rho_{31}. \tag{34}$$

As the expression in the square brackets is always positive, this implies that

$$\Im\mathrm{m}\ \rho_{31} = 0, \tag{35}$$

i.e. using (27-29)

$$\rho_{13} = \rho_{31} = \rho_{12} = \rho_{21} = \rho_{23} = \rho_{32} = 0. \tag{36}$$

On the other hand, from (33) and (35), we get that in the stationary state

$$\rho_{11} = \rho_{22}. \tag{37}$$

One should realize that conditions (37) and $\rho_{12} = \rho_{21}$ (see (36)) obtained so far fully correspond to what has been said above about no-flow equilibrium inside the dimer '1 - 2'.

The eighth or ninth equation of (16) yield, in the stationary state and with the help of (36),

$$\rho_{22} - \rho_{33} = 0. \tag{38}$$

Together with (20) and (25), it provides an inhomogeneous set of three linear algebraic equations determining the site occupation probabilities (all the time provided that the no-flow condition (24) used above applies). The solution reads

$$\rho_{11} = \frac{\Gamma_\downarrow}{\Gamma_\downarrow + 2\Gamma_\uparrow}, \quad \rho_{22} = \rho_{33} = \frac{\Gamma_\uparrow}{\Gamma_\downarrow + 2\Gamma_\uparrow}. \tag{39}$$

This result, on the other hand, contradicts (37). This is the required contradiction implying that (24) cannot be correct. One can also ask what is the reason for the contradiction. Clearly, (37) would be satisfied by (39) if there were $\Gamma_\downarrow - \Gamma_\uparrow = 0$. That would, however, mean to disregard the spontaneous processes that are responsible for the difference on the left hand side. The spontaneous processes are, however, purely quantum. Similarly, one can easily observe that (39) becomes fully compatible with (37) in the limit of the infinite temperature $T_{II} \to +\infty$. The infinite temperature limit means, however, the classical limit (the Bohr correspondence principle). All that is why we can understand the violation of the second law we arrive at below (as well as in other models yielding such a striking conclusion - see above) as a consequence of quantum effects.

So, there is always an electron circular flow in the system implying (not in general but) in our specific situation nonzero heat transfer $\mathcal{Q}$ (as given by (23) and (21) or (22)) between baths I and II. The last questions to be solved before we resort to a numerical study are what is its orientation and how the conclusion contradicts the second law.

V. VIOLATION OF THE SECOND LAW

In order to infer what is the orientation of the mean heat flow, let us turn to above formulae (21) and (23). From (23) we get that signs of $\mathcal{Q}$ and $\mathcal{J}$ coincide ($\epsilon_3 > 0$). As for the latter, we remind that ρ_{33} is always (as a site occupation probability) positive and that $\Gamma_\uparrow$ disappears for $T_{II} \to 0$. Thus, from (21), we get that $\mathcal{J}$ is, in the low temperature limit of bath II but arbitrary nonzero T_I, always positive. This is, by the way, also what our numerical results show.

Let us now increase T_{II}. One should realize that $\mathcal{Q}$ is a continuous function of T_{II} and never turns to zero. (For that, see the above proof.) So it should remain positive even when T_{II} becomes greater than T_I. (In fact, owing to intermixture of T_I with details of coupling to bath I in H^I_{S-B} inside Γ, nothing can happen at the moment when T_{II} passes T_I. This fact was also confirmed numerically.) Positive values of $\mathcal{Q}$ mean, however, a positive rate of heat transfer from bath I to bath II which thus goes, for $T_I < T_{II}$, *against* temperature step. As the heat transfer is spontaneous (there is no external expenditure of energy or whatever else conditioning this transfer), this conclusion explicitly contradicts the Clausius form of the second law [2] stating that such processes are impossible. On the other hand, the conclusion obtained analytically here (and verified numerically below) that the second law is in our system really violated fully corresponds to conclusions of [11] where, for an experimental plasma system corresponding to the above model, the universal validity of the second law was first seriously challenged.

VI. NUMERICAL RESULTS

In order to verify the above conclusions, we have solved the set (16) and (20) numerically. There was also a secondary reason for this numerical study: Analytically, we were unable

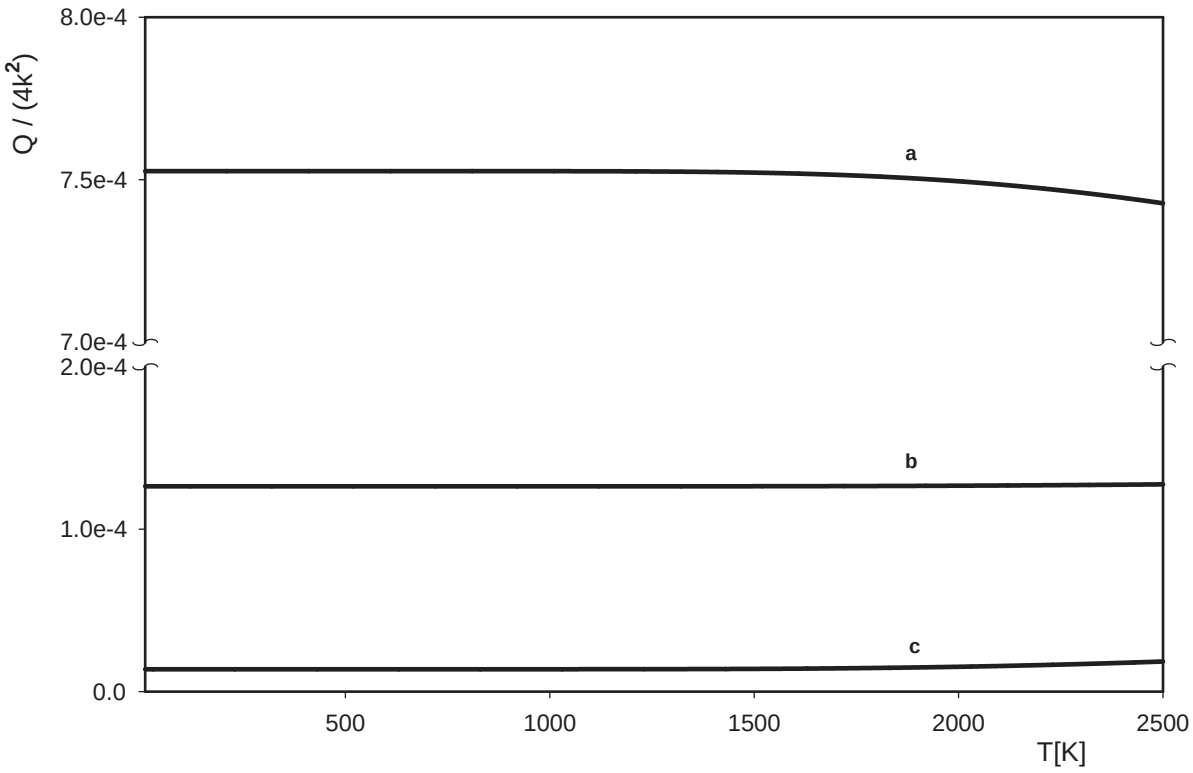

FIG. 1:

Figure 1: Spontaneous energy flow $\mathcal{Q}$ in units $4K^2/\hbar$ from bath I to bath II as a function of temperature $T_{II} = 1/(k_B\beta_{II})$ of bath II. We set here $J = K = 0.5$ eV, $\epsilon_2/K = 4$, $\epsilon_3/K = 2$, $\hbar\gamma_0/K = 0.02$, and $\hbar\Gamma/K = 10^{-2}$, 10^{-3} and 10^{-4} (decreasing dephasing rate, i.e. also heating, at site 1) for curves a), b), and c), respectively. Notice that 2Γ incorporates also temperature T_I of bath I.

to prove that the heat transfer really turns to zero in the limit of zero temperature T_I of bath I. This is what must be expected physically because in such a limit, there is no heat available in bath I to be transferred to bath II. In just other words: There is no dephasing in this limit between sites 1 and 2. So, the covalent bond 1-2 should become perfect, making thus the electron (and consequently also the heat) flow impossible.

Fig. 1 shows typical results. We designate $\gamma_0 = \Gamma_\uparrow[e^{\beta_{II}\epsilon_3} - 1]$. Three things are worth noticing:

- In accordance with the above analytical arguments, the mean heat flow $\mathcal{Q}$ is always positive (i.e. going from bath I to bath II).

- With decreasing dephasing rate 2Γ corresponding to decreasing temperature T_I, $\mathcal{Q}$

turns apparently to zero.

- For constant rate 2Γ, $\mathcal{Q}$ is only very little dependent on temperature T_{II} of bath II. Slight increase as well as decrease with T_{II} are both possible. This may be interpreted as a result of two competing tendencies:

  - Increasing T_{II} increases also the rate of dephasing between sites 2 and 3 caused by nonzero and T_{II}-dependent terms $-\frac{i\hbar}{2}\Gamma_{\downarrow}$ in 3-3 and 4-4 elements of block $\mathcal{C}$ in (16). Similarly the terms $-\frac{i\hbar}{2}\Gamma_{\uparrow}$ in 4-4 and 5-5 elements of block $\mathcal{A}$ in (16) contributing to dephasing of sites 1 and 2. This leads to greater violations of the 2-3 and 1-2 bonds, i.e. to increase of $\mathcal{Q}$.

  - Increasing T_{II} on the other hand implies relatively decreasing role of the spontaneous processes in $3 \to 1$ transitions what means suppression of $\mathcal{Q}$.

  Dependence of $\mathcal{Q}$ on T_{II} is, however, always very small.

VII. CONCLUSION

We have obtained a spontaneous heat flow between two *macroscopic* baths that is owing to a specific activity of our microscopic single-electron system not aided from outside. So, starting from rigorous mathematics of the quantum theory of open systems, a contradiction with the second law of thermodynamics has been obtained for the model in question. Remind that except for model assumptions, no approximations were made that could be made responsible for the effect, and that the model corresponds to an experimental system positively tested in [11]. This indicates that one should choose between just two alternatives:

- There is still something hidden in physics beyond the second law what is at present not fully understood. This possibility might also mean complementing contemporary quantum mechanics and present philosophy of quantum-mechanical modelling, to reconcile the quantum theory with (presumably) universally valid thermodynamics.

- The second alternative is to refrain from so far universally assumed validity of thermodynamics in the macroworld. One should realize that though our system is microscopic, appending the reservoirs turn the physics to the macroscopic one.

VIII. ACKNOWLEDGEMENT

The authors should like to acknowledge support from grants 202/99/0182 of the Czech grant agency and 153/99/B of the Grant agency of Charles University, Prague. V. Č. should also like to acknowledge discussions with D. P. Sheehan which he had during his visit to San Diego, and a previous collaboration with him that lead to paper [19] where similar ideas (though still without mathematical details) first appeared.

IX. APPENDIX

A. Derivation of basic kinetic equation from the Nakajima-Zwanzig identity

Scaling procedures of the above type are always an intricate and mathematically rigorous way of justifying, irrespective of the type of the scaling parameter used, the lowest order formulae in, e.g., kinetic equations. This does not mean, on the other hand, that such theories rely upon a possibility to use perturbation theory. Above, we have argued why we cannot apply the weak-coupling (to bath) scaling approach in our case. The reasons are:

- Its ability to include the bath-induced dephasing in the equations for the density matrix of the system but, simultaneously, its inability to incorporate, in the asymptotic time domain, its the effect on the *solution*, in particular on the site off-diagonal elements of ρ. [2] This dephasing is crucial for the effects investigated here as it conditions the existence of flows in our system.

- Its justification in just the regime where the bath-induced processes in the system are appreciably slower than all internal competing processes inside the system alone. However, we are here, in contrast to that, interested in situations where such processes are at least commensurable.

So we must refrain from the usual scaling (12) connected with identification (13) and use instead scaling (4) corresponding to choice (14). With that, one can start from, e.g., the

[2] One should realize that also, e.g., the Boltzmann equation includes the lowest-order scattering processes but its solution, e.g. the Fermi-Dirac distribution, is fully independent of details of the scattering and is correct to just its zeroth order.

Nakajima-Zwanzig identity [37, 38] for the density matrix $\rho^{S+B}(t)$ of the complex 'system + bath'. Introducing the density matrix of the complex in the interaction representation by $\tilde{\rho}^{S+B}(t) = \exp(i\mathcal{L}_0 t)\rho^{S+B}(t)$ and introducing correspondingly the Liouville superoperator $\tilde{\mathcal{L}}_1(t) = \exp(i\mathcal{L}_0 t)\,\mathcal{L}_1\,\exp(-i\mathcal{L}_0 t)$, the Nakajima-Zwanzig identity reads

$$\frac{d}{dt}\mathcal{P}\tilde{\rho}^{S+B}(t) = -i\mathcal{P}\tilde{\mathcal{L}}_1(t)\mathcal{P}\tilde{\rho}^{S+B}(t)$$

$$-\int_{t_0}^{t}\mathcal{P}\tilde{\mathcal{L}}_1(t)\exp_{\leftarrow}[-i(1-\mathcal{P})\int_{\tau_1}^{t}\tilde{\mathcal{L}}_1(\tau_2)\,d\tau_2]\,(1-\mathcal{P})\tilde{\mathcal{L}}_1(\tau_1)\mathcal{P}\tilde{\rho}^{S+B}(\tau_1)\,d\tau_1$$

$$-i\mathcal{P}\tilde{\mathcal{L}}_1(t)\exp_{\leftarrow}[-i\int_{t_0}^{t}(1-\mathcal{P})\tilde{\mathcal{L}}_1(\tau)\,d\tau](1-\mathcal{P})\tilde{\rho}^{S+B}(t_0). \qquad (40)$$

Now we set $t_0 = 0$, accept definition (7) and identification (14). For simplicity, we assume initial condition (9) where ρ^B appears also in the Argyres-Kelley projection superoperator (7). Because of that, $(1-\mathcal{P})\tilde{\rho}^{S+B}(t_0) = (1-\mathcal{P})\rho^{S+B}(0) = 0$ and, consequently, all the inhomogeneous initial-condition term (the last term on the right hand side of (40)) disappears. One can now introduce the new time t' by (see 14) $t' = t\cdot\lambda^2$ and use the identities

$$\mathcal{P}\tilde{\mathcal{L}}_1(t)\mathcal{P} = \mathcal{P}\frac{1}{\hbar}[\tilde{H}_S|_{J\neq 0\neq K} - \tilde{H}_S|_{J=K=0}, \ldots],$$

$$\mathcal{P}\tilde{\rho}^{S+B}(t) = \rho^B\exp\{\frac{i}{\hbar}[H_S|_{J=K=0}, \ldots]t\}\rho_S(t),$$

$$\mathcal{P}\tilde{\mathcal{L}}_1(t)\ldots = \mathcal{P}\frac{1}{\hbar}[\tilde{H}_{S-B}, \ldots] + \frac{1}{\hbar}[\tilde{H}_S|_{J\neq 0\neq K} - \tilde{H}_S|_{J=0=K}, \mathcal{P}\ldots]. \qquad (41)$$

Then we designate $\tilde{\rho}'(t') = \tilde{\rho}(t)$ in (40), divide the result by λ^2, take the trace Tr_B and take the limit $\lambda \to 0$. All but the lowest-order (in λ) terms disappear. Returning then to the Schrödinger picture by $\rho'(t') = \exp(-i\mathcal{L}_S t')\cdot\tilde{\rho}(t')$, $\mathcal{L}_S\ldots = \frac{1}{\hbar}[H_S|_{J=K=0}, \ldots]$, we obtain

$$i\frac{d}{dt'}\rho'(t') = \frac{1}{\hbar}[H_S|_{J\neq 0\neq K}, \rho'(t')] + i\mathcal{K}|_{J=K=0}]\rho'(t') \qquad (42)$$

what is nothing but, formally, (11) in the rescaled time. Anyway, there is one remarkable difference as compared to standard form of (11) with the Redfield form of the weak-coupling relaxation superoperator $\mathcal{K}$: Because of identities (41) and the limit $\lambda \to 0$, all the J- and K-dependent terms (J, $K \propto \lambda^2$) disappeared from the bath-induced-relaxation superoperator $\mathcal{K}$. That is why, in contrast to free propagation including particle transfer among extended eigenstates of $H_S|_{J\neq 0\neq K}$ (as described by the first term on the right hand side of (42)), the relaxation superoperator $\mathcal{K}$ does not include any J- or K-dependent (hopping) term (compare (1)). That is why the bath-induced relaxation goes among localized eigenstates of $H_S|_{J=K=0}$, i.e. sites.

B. Violations of the second law without scaling arguments

Arguments in favour of violation of the second law as reported above critically depend on the existence of the heat flow from bath I to bath II, i.e. on the existence of the electron mean circular flow $\mathcal{J}$. Existence of the flow has been above proved using scaling which does not belong to a generally accepted weaponry in kinetic theories. Moreover, one could ask about justification to use such a (as well as any other) kinetic approach beyond limits of the kinetic regime. (Notice, e.g., that constant a in $...\sup_{0\leq\lambda^2 t\leq a}...$ in (8) is always finite.) That is why, technically using the above formulae, arguments in favour of existence of nonzero values of $\mathcal{J}$ are given below that do not rely on scaling arguments employed above. Though we insist that the above arguments are mathematically rigorous (i.e. that the above treatment is free of any additional approximations imposed on the assumed model), the treatment below is even more straightforward. One should add that, in our opinion, the only acceptable potential objection to *all* kinetic treatments (including those connected with the weak-coupling scaling like theories based on the Boltzmann or Pauli equations) is that they might become dubious in the very-long-time asymptotics. As standard practice with, e.g., the Boltzmann theory in the dc limit shows, this may rather concern the asymptotic way of approaching stationary states than the very form of the asymptotic distributions which is currently reproduced in accordance with standard equilibrium statistical physics. The treatment below is resistive even against such objections as it assumes, as experiments require, taking first the dc limit. *Only then* (if at all) discussion based on smallness of individual terms in the Hamiltonian (coupling constants etc.) comes into question.

In the Schrödinger picture, the Nakajima-Zwanzig identity (40) reads [37, 38]

$$\frac{d}{dt}\mathcal{P}\rho^{S+B}(t) = -i\mathcal{P}\mathcal{L}\mathcal{P}\rho^{S+B}(t) - \int_0^t \mathcal{P}\mathcal{L}\mathrm{e}^{-i(1-\mathcal{P})\mathcal{L}\cdot(t-\tau)}(1-\mathcal{P})\mathcal{L}\mathcal{P}\rho^{S+B}(\tau)\,d\tau$$
$$- i\mathcal{P}\mathcal{L}\mathrm{e}^{-i(1-\mathcal{P})\mathcal{L}\cdot t}(1-\mathcal{P})\rho(0). \tag{43}$$

Using the Argyres-Kelley projector (7) and initial condition (9), it yields for the density matrix $\rho(t)$ of the system

$$\frac{d}{dt}\rho_{mn}(t) = -i(\mathcal{L}_S\rho(t))_{mn} + \int_0^t \sum_{p,q} w_{mn,pq}(\tau)\rho_{pq}(t-\tau)\,d\tau. \tag{44}$$

Here

$$w_{mn,pq}(\tau) = -\langle m|\mathrm{Tr}_B\{\mathcal{L}\mathrm{e}^{-i(1-\mathcal{P})\mathcal{L}\cdot(\tau)}(1-\mathcal{P})\mathcal{L}(\rho^B\otimes|p\rangle\langle q|)\}|n\rangle \tag{45}$$

are the memory functions whose decay in time is owing to dephasing in the bath. Now we take the infinite (thermodynamic) limit of the bath(s) (designated as Lim below) and let time t increase to infinity. In the full long-time domain we are here interested in, relaxation to stationary state of the system takes place, i.e. not the interaction-picture density matrix of the system $\tilde{\rho}(t)$ but the Schrödinger picture density matrix $\rho(t)$ becomes stationary. Designating its long-time limit as above as just ρ, (44) turns for our model to

$$0 = -\frac{i}{\hbar}\sum_{r=1}^{3}[(H_S)_{mr}\rho_{rn} - (H_S)_{rn}\rho_{mr}] + \sum_{p,q=1}^{3} W_{mn,pq}\rho_{pq},$$

$$W_{mn,pq} = \int_0^{+\infty} \mathrm{Lim}\, w_{mn,pq}(\tau)\, d\tau \quad m, n = 1, 2, 3. \tag{46}$$

For our situation, this is the set of 9 equations with the rank equal to just 8. This is because of identity $\sum_m W_{mm,pq} = 0$. (This identity is a consequence of the rule $\sum_m w_{mm,pq} = 0$ following from (45) ensuring that the total probability $\sum_m \rho_{mm}(t)$, being initially equal to 1, remains time-independent.) So, we may omit the first equation of (46) for $m = n = 1$, replacing it by the normalizing condition (20) above. This yields (in an analogous way as above) a set of inhomogeneous linear algebraic equations

$$\begin{pmatrix} \mathcal{E} & \mathcal{F} \\ \mathcal{G} & \mathcal{H} \end{pmatrix} \cdot \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \\ \rho_{12} \\ \rho_{21} \\ \rho_{13} \\ \rho_{31} \\ \rho_{23} \\ \rho_{32} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \tag{47}$$

where the blocks in

$$\mathcal{S} = \begin{pmatrix} \mathcal{E} & \mathcal{F} \\ \mathcal{G} & \mathcal{H} \end{pmatrix} \tag{48}$$

are given as

$$\mathcal{E}=\begin{pmatrix} 1 & 1 & 1 & 0 & 0 \\ W_{22,11} & W_{22,22} & W_{22,33} & W_{22,12}-iJ/\hbar & W_{22,21}+iJ/\hbar \\ W_{33,11} & W_{33,22} & W_{33,33} & W_{33,12} & W_{33,21} \\ W_{12,11}+iJ/\hbar & W_{12,22}-iJ/\hbar & W_{12,33} & W_{12,12}+i\epsilon_2/\hbar & W_{12,21} \\ W_{21,11}-iJ/\hbar & W_{21,22}+iJ/\hbar & W_{21,33} & W_{21,12} & W_{21,21}-\epsilon_2/\hbar \end{pmatrix},$$

$$\mathcal{F}=\begin{pmatrix} 0 & 0 & 0 & 0 \\ W_{22,13} & W_{22,31} & W_{22,23}+iK/\hbar & W_{22,32}-iK/\hbar \\ W_{33,13} & W_{33,31} & W_{33,23}-iK/\hbar & W_{33,32}+iK/\hbar \\ W_{12,13}+iK/\hbar & W_{12,31} & W_{12,23} & W_{12,32} \\ W_{21,13} & W_{21,31}-iK/\hbar & W_{21,23} & W_{21,32} \end{pmatrix},$$

$$\mathcal{G}=\begin{pmatrix} W_{13,11} & W_{13,22} & W_{13,33} & W_{13,12}+iK/\hbar & W_{13,21} \\ W_{31,11} & W_{31,22} & W_{31,33} & W_{31,12} & W_{31,21}-iK/\hbar \\ W_{23,11} & W_{23,22}+iK/\hbar & W_{23,33}-iK/\hbar & W_{23,12} & W_{23,21} \\ W_{32,11} & W_{32,22}-iK/\hbar & W_{32,33}+iK/\hbar & W_{32,12} & W_{32,21} \end{pmatrix},$$

$$\mathcal{H}=\begin{pmatrix} W_{13,13}+i\epsilon_3/\hbar & W_{13,31} & W_{13,23}-iJ/\hbar & W_{13,32} \\ W_{31,13} & W_{31,31}-i\epsilon_3/\hbar & W_{31,23} & W_{31,32}+iJ/\hbar \\ W_{23,13}-iJ/\hbar & W_{23,31} & W_{23,23}-i(\epsilon_2-\epsilon_3)/\hbar & W_{23,32} \\ W_{32,13} & W_{32,31}+iJ/\hbar & W_{32,23} & W_{32,32}+i(\epsilon_2-\epsilon_3)/\hbar \end{pmatrix}. \tag{49}$$

Our set (47) (with (48-49)) should now be solved by the Kramer rule and the result should then be put into (22) to check whether the electron circular flow $\mathcal{J}$ and, consequently, also the heat transfer $\mathcal{Q}$ are nonzero in the stationary situation or not [3]. One should stress here that formula (22) is [in contrast to (21)] independent of the above scaling treatment, fully corresponds to the standard electron flow formula of the quantum mechanics, and may also be easily derived from, e.g., the population balance $\frac{d}{dt}\langle a_2^\dagger a_2\rangle$.

All the formulae now become totally unwieldy and, in addition to it, there are big technical problems with calculation of $W_{mn,pq}$ coefficients. So, we shall limit here to what is for our

[3] See [39] for the case that the Kramer rule yields uncertain expression of the type '0/0'.

purposes sufficient. This is discussion of limiting situations which allows, owing to continuous dependence of solutions of inhomogeneous sets of linear algebraic equations on its coefficients and also that of the latter coefficients on the parameters of our model, at least qualitative statements we need.

Weak-coupling limit: In contrast to standard practice of kinetic equations but fully in accordance with what experiment requires, we take here the limit of weak-coupling to bath H_{S-B} only *after* taking the dc limit. (Remember that in experiment, frequency may be set arbitrarily low, or time may be taken arbitrarily large. On the other hand, all coupling constants including that of H_{S-B} are in Nature always finite though possibly small. That is why, e.g., they could be set small in asymptotic expansions only, if at all, i.e. after performing the dc limit as we do here.) Performing the second-order (in H_{S-B} coupling) expansion of $W_{mn,pq}$ allows to express them in an explicit form. The latter, however, involves exact energies and exact eigenstates of H_S that can be made explicit in our three-site model only via Cardano formulae for solution of the algebraic equations of the third order. (Notice that otherwise, H_S cannot be explicitly diagonalized.) That is why we shall refrain here from explicit formulae for the second-order approximants $W^{(2)}_{mn,pq}$ of $W_{mn,pq}$. Replacing $W_{mn,pq}$ by $W^{(2)}_{mn,pq}$ in (47), however, one can as usual verify (as it also follows from arguments of standard equilibrium statistical physics) that formally (invoking standard perturbational arguments)

$$\rho = \sum_{\iota=1}^{3} |\iota\rangle p_\iota(\beta_I, \beta_{II}) \langle\iota| + \mathcal{O}((H_{S-B})^2). \tag{50}$$

In our case here, because of existence of two (say warmer and colder) baths, real probabilities $p_\iota(\beta_I, \beta_{II})$ have in general not the usual simple canonical form but another more complicated one, involving both initial bath temperatures. They may also depend on the relative ratio of the two terms in H_{S-B} in (3) coupling the electron to baths I and II, respectively. The states $|\iota\rangle$ are eigenstates of H_S. What is important is that the leading first term on the right hand side of (50) (i.e. the canonical density matrix in the case when $\beta_I = \beta_{II}$) represents ρ just in the zeroth order in the coupling to the bath. To this order, in our real basis of localized states (sites) $|m\rangle$, $m = 1, 2, 3$, $\rho_{12} = \rho^*_{21}$ becomes thus, according to (50), real in the weak-coupling limit. Thus, according to (22), there should be no electron flow and, consequently, also no electron-mediated heat transfer between our bath. Thus, no contradiction with the second law appears

in the zeroth order in the coupling to the bath. This is *fully in accordance with the standard weak-coupling kinetic theory.* On the other hand, for general situation, *this conclusion* valid only in the extreme weak-coupling limit *means practically nothing.* The point is that the effect we are looking for may appear just when corrections to the lowest (zeroth) order form of ρ in (50) implying, *inter alia*, perturbations of otherwise stiff intersite covalent bonds get included. In order to convince the reader, we come to more general considerations.

Outside the weak-coupling limit: For simplicity, let us set $K = J$ in what follows here. Apart from other parameters, the flow (22) thus depends, via the solution to (47), on both J and the system-bath coupling constant, say λ. As far as we accept $J = c \cdot \lambda^2$, we can, allowing λ to approach zero, move to zero in the J-λ plane along many routes according to choice of the constant c. [One should compare the approach with (4); here, however, we have already turned, as one in fact should as argued above, our time t to infinity.] Let us remind the reader that the above weak-coupling case would correspond to approaching arbitrary point outside origin on the J axis and only then, if at all, to approach origin along the J-axis. The fact that we got zero electron flow in such a limit indicates nothing for a general case, in the same way as the fact that

$$\lim_{y \to 0} x^2 y^2 = 0 \tag{51}$$

and zero small-x expansion (asymptotics) of $g(x) = lim_{y \to 0} x^2 y^2 = 0$ does *not* imply that $f(x, y) = x^2 y^2$ equals to zero in the $x - y$ plane. Nonzero values of $f(x, y)$ in the vicinity of origin $x = y = 0$ may be, however, seen from the fact that on, e.g., the parabola $y = \lambda$, $x = c \cdot \lambda^2$, we get nonzero asymptotics of $f \approx_{\lambda \to 0} d \cdot \lambda^6$ with nonzero proportionality constant d. By calculating such an asymptotics is how we shall proceed now.

Let us expand now, taking into account $J \propto \lambda^2$ and $H_{S-B} \propto \lambda$, coefficients $W_{mn,pq}$ in (47) to the second order in λ. For the lowest-order approximants for the ρ_{mn} elements, one in fact obtains, after a long but straightforward algebra, exactly the same set of equations as obtained above from (16) by setting the left hand side zero and replacing the first equation by (20). This set has already been treated in detail, both analytically and numerically, above. So we can directly use the results. In

particular, from this set, we obtain as above proper (small-λ) asymptotics of ρ_{mn} with (for correspondingly nonzero though at least sufficiently small λ) nonzero values of the flow in (22). Accordingly, we also obtain like above nonzero values of heat flow $\mathcal{Q}$ in (23) implying, for $T_I < T_{II}$, violations of the second law. Hence, in general points around origin in the $J \equiv K$ vs. λ plane and except for coordinate axes corresponding to exactly zero hopping integrals $J = K = 0$ or zero order in the coupling to the bath (when (50) implies the canonical form of ρ), the second law of thermodynamics cannot be in general preserved. This is in a full accord with our result in the main text.

One should again stress that this method allows to avoid the scaling arguments at all and is more honest as compared to experiment by first turning the time to infinity and only then investigating the proper asymptotics for the heat transfer between our two baths.

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